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LEAD TELLURIDE NON-MAGNETIC BONDING
RESEARCH STUDY

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ABSTRACT

The purpose of this study is to define in fundamental terms the most appropriate system and process for the reproducible fabrication of low-resistance, high-strength bonds of non-magnetic electrodes to PbTe and PbTe-SnTe thermoelectric alloys. Investigations during this period have covered the following areas: precision of thermoelectric property measurements has been evaluated; thermoelements have been studied physically and by chemical analyses; procedures have been refined for diffusion bonding of W to n-type PbTe and the effects of bonding on thermoelectric properties and effects of some process variables evaluated; the effect of temperature on the contact resistance of W on PbTe was studied; diffusion bonding and SnTe brazing of p-type PbTe-SnTe to W was studied; metallographic techniques were developed for examination of unbonded and bonded structures.

I. INTRODUCTION

The widespread use of thermoelectric power generation has been anticipated for some years as the solution to a number of power-supply problems. Two major materials problems have, however, hindered the application of thermoelectrics. The first problem is associated with the bulk material; because of the predominantly covalent nature of most thermoelectric alloys, they tend to be weak and brittle. The presence of doping agents severely limits the use of normal fabrication by casting because of segregation of the dopants, and thus a majority of commercially available thermoelements have been produced by powder metallurgical techniques. However, pressed and sintered compacts are usually porous to some extent, contain oxides and other particulate inclusions, forces within the compacting die cause variations in density through the compact which can lead to discontinuous grain growth during sintering, and it is not unusual for the internal pores to contain gases which, if they include oxygen, can cause oxidation during service.

Compounded with these problems is the second major difficulty of making satisfactory electrical and thermal contact to the thermoelement. A number of different approaches have been taken to provide low resistance, stable contacts to thermoelements under varying conditions of temperature, etc. These can be divided generally into methods which maintain contact mechanically, as by spring-loading, and those which employ an integral electrode, usually metallurgically bonded. The former add considerable size and complexity to the module system, while the latter, although more elegant and efficient, are most severely troubled by problems of material incompatibility. Among the important requirements for a suitable electrode is that it not react with the elements to form low-melting compounds, etc.; that the metal not be electrically active if it diffuses into the element; that the coefficient of expansion of the metal approximates that of the semiconductor element; and that it will initially form a strong, low-resistance bond to the element. Some advantages can be gained by the use of a suitable intermediate braze, which, most importantly, can provide a gradation in properties between electrode and element. Once again, however, there are several restrictions on the braze material if it is to provide a satisfactory bond.

The present program comprises an investigation of the bonding of PbTe thermoelements to non-magnetic electrodes, and a study of the physical and chemical factors contributing to the degradation and failure of such thermocouples during extended operation. Under a previous contract with this laboratory (NAS5-3986) a number of systems were investigated as potential electrode-braze combinations. Tin telluride braze on a Ta electrode was found to be most satisfactory with PbTe-SnTe elements, while a pressure-diffusion bonding process of W with n-type PbTe showed more promise than any of the brazes. These two bonding processes were taken as a departure point for the current program with the aim of refining the procedures to produce consistently low-resistance, high-strength bonds and then studying their behavior at elevated temperatures.

II. THERMOELEMENT EVALUATION

Both phases of this investigation are, to a greater or lesser extent, concerned with questions of a "before and after" nature. "What are the effects of bonding procedures?" is answered by showing the element as it was prior to bonding and then after. "What are the effects of extended operation at high temperatures?" asks primarily what was the element like when it was fabricated, and what is it like after, say 2000 hours at 600°C. It is obvious that precise, reliable measurements or observations of electrical and physical properties of the thermoelements are of considerable importance in any such studies.

A. Electrical Measurements

The thermoelectric power and resistivity are not only the most important parameters of a thermoelectric material, but are also most sensitive to processes which are otherwise below the threshold of detection by other means. A series of measurements of room temperature resistivity, variation of resistivity with temperature, and Seebeck voltage versus temperature were made on unbonded n- and p-type elements (Minnesota Mining and Manufacturing Company 3NB and 3PB). These measurements sought to establish the precision of the three techniques, and to provide a group of elements with well-established properties for further experimentation.

1. Room Temperature Resistivity

A four-point probe device with one moveable voltage probe has been used to measure room temperature resistivities of elements and contact resistivities of bonded elements. The results of a large number of measurements on different types of elements indicate a rather large random error in the technique. The average standard deviation from five sets of measurements is 25% of the value of the mean. As a test of the source of the error, a group of seven elements were measured; then one element, selected at random, was measured seven times. The average resistivity values differed by 1.5% between the group and the single element. The standard deviations were identical. This indicates that most of the random error is in the apparatus, for, had the elements been highly variable, the error in the measurement of the single element would have been much lower. The variation in the measurement is apparently due to a combination of random effects in loading the sample in jig, in the "efficiency" of the contacts, and in the operation of the electronics. The resistivity is calculated in a way so as to cancel the effects of contact resistance at the voltage probes, except for the case of the moveable probe having a variable resistance from point to point. However, measurements on metallic samples indicate that this effect should be more than an order of magnitude lower than the resistances being measured.

Contact resistivities of bonded elements are determined by measuring the resistance at 25 mil intervals across the bond and along the element, and then extrapolating the plot of resistance vs. distance to the point of the bond. Contact resistance is taken as the discontinuity in the plot at this point. Each bond is measured twice, once with the moveable probe going from electrode to element, and in the opposite direction; the average of these values is then used for calculating the resistivity.

2. Variation of Resistivity with Temperature

The apparatus for these measurements has been described in an earlier report ⁽¹⁾. A recent modification has made possible the reproducible measurement of resistance with temperature of unbonded elements. Where the apparatus previously used needle-like tungsten voltage probes, the same

probes with their points bent into semicircles can now bear directly on the thermoelement without fracturing the material under the probes. This configuration of the probes provides a reliable, low-resistance contact over the entire temperature range of measurements. Using this technique, a series of measurements was made with the same elements mentioned above. Averaged curves of resistivity vs. temperature were calculated from single measurements of six samples and six measurements of a single sample. The average difference between the two curves was 4%, which should roughly represent the deviation of the single sample from the average value for the entire lot, while the average standard deviations for the two curves were almost the same, 22 and 20%. The average curve for the six samples is shown in Fig. 1 with the nominal curve for the material published by Minnesota Mining and Manufacturing (3M). Figure 2 shows the results for similar measurements on a group of p-type elements. The difference between the nominal curve and our measurements is greater here than for the n-type elements; however, such discrepancies are felt to be of little importance, for they can, in part, be attributed to lot-to-lot variations in properties, and more basically, the important differences, for our purposes, are those between samples at one stage, and after some treatment.

The important conclusion to be drawn from these measurements is that the method and/or apparatus is inherently too variable for any single measurement to have any significance, but that repetitive measurements on a single sample, or measurements of a number of similarly-treated samples can provide meaningful information on changes in resistivity in the area of 5% or greater.

3. Seebeck Voltage

The precision of the Seebeck voltage measurement has been fairly well assessed by two sets of measurements on new elements. Figures 3 and 4 show the average curves for n- and p-elements respectively, with the nominal curves for the materials. The vertical bars on the experimental lines indicate one standard deviation. For n-type elements the standard deviations over the range 250° to 500° was 5%. Over the same temperature range, the p-type material showed a standard deviation of less than 2%. These figures must represent variations of the order of the piece wise variation

in properties; so it would be reasonable to assume that the variation in the measurement itself is, perhaps, 1% or less.

B. Physical-Metallurgical Evaluation

The elements supplied by Minnesota Mining and Manufacturing are fabricated by cold-pressing and sintering a powder of the desired composition. As was noted in the introduction, this process can result in a less than wholly desirable structure. Figures 5 and 6 show macro- and microsections of n-type and p-type elements, respectively. The microsections are of areas selected at random in the centers of the elements. The dark areas are pores. The pores appear as white specks in the macrophotos 5a and 6a. It is interesting to note that the n-type element shows large pore-free areas, which one might call "pseudo-grains", for they are actually made up of a number of smaller, real grains as shown in the etched microsection of Fig. 7, while the pore-structure of the p-type element shows much less regularity. The difference would seem to be the result of a lower compacting pressure and lower sintering temperature for the p-type material. The type of grain growth seen in Fig. 7 within the large pseudo-grain is much less prevalent in p-type elements (see Fig. 8), although this may be due to the greater amount of porosity which immobilizes most of the grain boundaries early in the sintering process. It is of some importance to note that in both materials the amount of porosity present should provide a considerable impediment to further grain growth at temperatures likely to be encountered in service, for most grain boundaries have already been tied up by pores and inclusions, and this has occurred at a fairly high temperature, so that the driving forces present at service temperatures will very likely be too small for any significant increase in grain size. No significant grain growth was found in annealing n-type elements 1500 hours at 540° C and 855 hours at 650°C in a 1961 study at Atomics International (2).

Density measurements on a number of n- and p-type elements from three different lots of each type support the microstructural evidence of considerable porosity. N-type PbTe elements are 97% of theoretical density with surprising consistency. P-type elements are about 90% of theoretical density, assuming a composition of 0.5 PbTe-0.5 SnTe. The p-type material

was somewhat more variable in density, ranging from about 88% to 91% of theoretical. The density found for the n-type elements indicates some improvement in their manufacture, since the above-mentioned study ⁽²⁾ measured 94% for n-type in 1961. A recent report by Hittman Associates, Inc. ⁽³⁾ describes hot-pressing of 3M powder of the 2N and 2P compositions which yields elements with densities in excess of 97% (how much in excess is not stated) and shows very little porosity compared to 3M-prepared elements.

C. Chemical Analyses

To date, wet chemical analysis and vacuum fusion gas analysis have been performed on n- and p-type elements. Wet chemical analysis gave the over-all compositions of the elements, indicating n-type to be PbTe and p-type to be approximately 0.44 PbTe - 0.56 SnTe. Vacuum fusion analyses were done twice, the first time using a conventional iron-carbon bath, which gave considerable difficulty due to the high vapor pressure of PbTe and SnTe; the second analysis was done with a bath of copper-nickel-carbon. The results are summarized in Table I below.

TABLE I
Gas Content of N and P Thermoelements
by Vacuum Fusion Technique

| | <u>3N</u> | | <u>3P</u> | |
|----------------|------------|------------|------------|------------|
| | <u>1st</u> | <u>2nd</u> | <u>1st</u> | <u>2nd</u> |
| O ₂ | -- | 80 ppm | 540 | 270 |
| N ₂ | -- | n. f. | 30 | n. f. |
| H ₂ | -- | n. f. | 2.3 | < 1 |

The principal gaseous impurity is apparently oxygen, and it is present in at least three-times greater quantity in p-type elements than in n-type. There is no particular reason to expect this result, but it is interesting to speculate on the relative amounts of porosity, p-type containing about 10% and n-type about 3%. The ratio being the same in both cases might indicate a relation between the porosity and the oxygen content.

III. BONDING STUDIES

The exploratory investigations under Contract NAS 5-3986 indicated that pressure or diffusion bonding could produce low resistance, high strength bonds which did not adversely affect the thermoelectric properties of the elements when W was joined to PbTe and PbTe-SnTe elements. It was also found that SnTe braze on Ta electrodes provided satisfactory bonds to PbTe-SnTe. The present effort aims to define the most appropriate system and process for reproducible fabrication of satisfactory bonds to PbTe alloys. It was felt that the systems previously investigated held the most promise; therefore, studies of bonding have been generally directed to refining procedures to increase the quality and reproducibility of the bonds. During this period the use of Ta electrodes for PbTe-SnTe has been provisionally discarded to concentrate on bonding to W. The advantages of a common hot-shoe of the same material are obvious, and the previous study had shown the feasibility of diffusion-bonding PbTe-SnTe to W. Thus, the present bonding studies are intended mainly to "clean up" the processes and study the effects of a few of the major variables in the bonding processes; however, further clarification of the Ta braze bonding process will be attempted in the next quarter.

A. N-type PbTe to Tungsten

Two important variables in the bonding process were studied in detail: surface preparation and pressure. Other variables studied were time at bonding temperature and loading procedures.

1. Surface preparation: In the initial runs the electrodes within a run were lapped to different grits, so that elements were bonded under identical conditions while the surfaces of the electrodes ranged from 180 to 1800 grit. The results of these runs indicated that the choice would be between the two extremes, 180 and 1800 grit; thus, subsequent runs were made using these two degrees of surface finish. The surfaces of all elements were lapped to 1800 grit, and the position of elements in the bonding jig were randomized to minimize any positional effects. The primary means of evaluating the bonds was the room temperature resistance or contact resistivity. The results of this study indicate that electrodes lapped to 180 grit provided higher quality; i.e. lower resistance bonds than 1800 electrodes, under the

same conditions. This is, in part, an indication that the flatness of the electrode surface is of greater importance than the roughness, and that the flatness is not improved by further lapping beyond the first step. It is also reasonable to assume that the rough surface produced by 180 grit would aid in penetrating oxide films on the PbTe surface and would produce a mechanical "keying" effect which would be much less prevalent in an 1800 grit bond.

2. Pressure: Experiments employing different pressures for diffusion-bonding of W to PbTe indicate that pressure alone is not of great importance in fabricating low-resistance bonds. Carefully controlled experiments using pressures of 50 and 200 gm/cm² show no significant difference in bond resistivities, although other experiments indicated a substantial improvement in bond resistivity when the higher pressures were used. It is felt that this was due to the greater ability of the higher pressures to overcome misalignments and mechanical hindrances of the components. With the elimination of these random constraints we have seen that pressures of 50 gm/cm² can produce bonds of $5 \mu \Omega \text{ -cm}^2$ as reproducibly as 200 gm/cm².

However, the use of pressures as high as possible without causing excessive gross deformation of the thermoelement is recommended for its contribution to better reproducibility.

3. Loading procedures: The above findings were made possible by a careful examination and elimination of various factors which could interfere with the bonding process. It was found that the bottom (in the bonding jig) contact was of a lower-resistivity than the upper bond - this was revealed by averaging results of so many different conditions that it had to be the result of some uncontrolled variable. Examination of the electrodes showed a small burr from the cutting operation; this burr was probably catching the side of the hole and tipping the electrode slightly. This didn't effect the bottom electrodes, since the cut face (with the burr) lay at the bottom of the hole. Lapping both faces of the electrode eliminates the burr. Elements are now loaded in the bonding jig assembly so as to prevent the exposure of the bond surfaces to the possibility of bits of graphite scraped from the side of the hole falling onto the surface of the element or electrode.

4. Time: From experiments in which the time at bonding temperature has differed by slightly more than a factor of two; 20 to 45 minutes, it appears that the bonding process is not very sensitive to time. A more thorough investigation with a variation of six times or more is necessary to reach a definite conclusion. At times of greater than an hour, any additional benefits would very likely be offset by sublimation losses from the element.

5. Braze-bonding: Although the preliminary study had shown the diffusion process to be superior to any brazes for n-type elements, another system was tested to investigate the possibility of using a combination braze-diffusion process to bond n-type PbTe to W. Chunks of PbTe were melted onto lapped W electrodes. Then the PbTe was lapped flat. The PbTe "braze" was then bonded, by diffusion, to the element using the same time-temperature cycle as is used for W diffusion bonding. Because of inconsistent wetting of the W by the PbTe and the high resistivity of the bonds produced, this investigation was abandoned.

6. Effect of bonding on electrical properties: The changes in thermoelectric properties due to bonding are not entirely clear. Data on room temperature resistivity for one group of elements indicate an average 17% decrease after bonding, while data from a larger sample shows a 5% increase with bonding. Because of differences in bonding variables and other factors, the data are not strictly valid; and until elements all prepared similarly can be measured the question must be kept open. Figure 9 shows the results of some fairly careful measurements on a group of quite similar elements (all had both contacts $< 40 \mu \Omega \text{-cm}^2$). The bonded elements were measured with the voltage probes on the element proper. It is felt that these results are indicative of the actual effects of bonding in sign and magnitude.

Figure 10 shows the effect of bonding on the Seebeck voltage. The curve for bonded elements represents the average of twelve doubly-bonded elements. These results are believed to represent with reasonable accuracy the effect of bonding on the Seebeck output; although the curves are within each other's experimental error (the vertical bar represents one standard deviation), the curve for bonded elements lies just outside the one standard deviation limit of the average new element curve, so the difference is meaningful.

B. P-type PbTe-SnTe to Tungsten

1. Diffusion bonding: Although as reported previously ⁽¹⁾ no important differences were observed in the bonding of p- as well as n-type material, during this period, experiments to optimize procedures for diffusion bonding of PbTe-SnTe to W electrodes have met with considerable difficulty. Very few elements have bonded at all, while those which did had high resistivity, low strength bonds. All the important variables of the process were varied over their full range. Pressures from 50 to 500 gms/cm² were used, all degrees of surface preparation were tried, and both static and flowing inert atmospheres were used. The appearance of the electrode surface and the surface of the W weights indicate that oxygen, apparently from the element, oxidizes the electrode before bonding can occur. It was noted previously that p-type elements were found to contain about 300 ppm oxygen. This was found in a batch which was used for a number of non-bonding experiments, and the few elements which were bonded could not be relied on to indicate whether this oxygen level was significantly interfering with bonding. However, since the initial part of the program showed that W could be bonded quite satisfactorily to PbTe-SnTe elements, it seems safe to state that the present difficulty is not due to any inherent incompatibility of the materials or maladjustments of the process. Attempts to make a degassed, densified sample of the 3M PbTe-SnTe by vacuum melting of the elements has not yet yielded a satisfactory piece. Adequate bonding of such a piece would tend to indicate that a gaseous impurity was at fault. Elements which were held at 300°C under vacuum for 60 hours were the first from two lots of material which showed any tendency to yield diffusion bonds; one contact had a resistivity of $30 \mu\Omega\text{-cm}^2$.

2. SnTe brazing to tungsten: As an alternative procedure for bonding p-type elements to W, the use of SnTe braze has been re-evaluated. Previously, the SnTe-W combination was discarded in favor of SnTe-Ta, which showed superior wetting. It has been found that the process of heating the W electrodes to 1200°C under vacuum to volatilize the oxides, and then evaporating a protective layer of Sn, gives excellent wetting when the braze is subsequently melted on. Bonds were made with these brazed electrodes to elements which had shown no inclination to bond by diffusion. Electrodes with a layer of SnTe evaporated onto the contact surface after deoxidizing

failed to bond when matched with elements from the same lot. Thus, it would appear that use of a thick braze layer will prevent oxygen from the element from reaching the electrode during the time required for bonding. Very probably the oxygen would diffuse through the braze under service conditions and eventually destroy the braze-electrode bond. Thus, the use of a braze cannot be regarded as the solution to a problem that lies basically with the purity of the material in the element.

C. Contact Resistivity

The major aim of the refinement of bonding procedures is to produce low resistance bonds. This has been fairly well accomplished for n-type elements. In a run at the end of the bonding investigation five bonds (out of twelve) had resistances of $5\mu\Omega$ or less. A question remained unanswered with respect to the behavior of contact resistance with temperature. Measurements had not been possible because of the difficulty of making a reliable contact directly to the element. A recent paper by Jain and Berry⁽⁴⁾ showed that the resistances (resistivity) of iron contacts on PbTe did vary with temperature, and that the temperature dependence of the resistivity was of the form $\rho_c \propto T^x$ with x approximately equal to 2.5. They explain their results on the basis of an idealized model of the contact potential barrier.

For the present measurements five W-bonded n-type PbTe elements (bulk resistivity approximately $0.490\text{ m}\Omega\text{-cm}$ at room temperature) with bond resistivities of about $40\mu\Omega\text{-cm}^2$ on both electrodes were selected. Elements with fairly high contact resistivities were chosen in order that the variation might be more easily detected. The change in resistance with temperature was measured twice for each element: once with the voltage probes on the element, the second time with the probes on the electrodes to include the contact resistance. The two sets of curves were averaged and the difference between them was taken as the total contact resistance. The contact resistivity was calculated by taking one-half the total average contact resistance and multiplying by the area of the contact. The results are plotted in Figs. 11 and 12. Figures 13a and 13b show the bulk resistivity as function of temperature (Fig. 9 replotted) for unbonded and bonded elements. The general agreement among the slopes (the temperature exponent x in $\rho_c \propto T^x$) indicates agreement with Jain and Berry who found that the temperature dependence of the contact resistivity was approximately the same as that of the bulk mobility.

As they stand, our data allow some tentative predictions to be made concerning the contact resistance contribution to total element resistance. Extrapolating to a room temperature contact resistivity of $5 \mu\Omega\text{-cm}^2$, we find the contact resistance at 500° to be about $0.2 \text{ m}\Omega$ for a 0.250 inch diameter element. Measurements have not yet been made to substantiate this.

IV. METALLOGRAPHY

A. Procedures

Metallographic preparation of brittle, low-hardness material such as PbTe is generally difficult and, in the case of bonded structures, is further complicated by the presence of the electrode. The juxtaposition of two materials of widely differing hardness will, at best, result in the softer material being polished away more rapidly. It has been our experience with bonded PbTe structures, and of other workers in this laboratory with systems such as boron-tin, that normal polishing procedures tend to produce a groove at the interface between the two materials; see Fig. 14. This, of course, obscures the area of greatest interest for this study. It was felt for some time that the presence of this groove indicated that the bond either occurred as only limited areas of contact while the major portion was simply a hole, or that a diffusion layer was formed of very brittle or very soft material. While the latter may still be in part true, examination of a number of bonds which had not been polished indicates that contact is widespread and quite intimate for low resistance bonds; see Fig. 15. Intersections of pores with the element surface leave uncontacted areas, as would be expected. The area uncontacted due to the presence of pores is equivalent to the volume fraction of pores; thus, in a 95% dense material a perfect diffusion bond still leaves some 5% of the electrode uncontacted.

A procedure has been developed for preparing bonded PbTe elements such that the element can be examined optically and photographed to within one or two microns of the interface of electrode and element. Coarse and fine grinding are done with SiC papers through 600 grit. Polishing is done with emery papers 2/0, 3/0, and 4/0 on a glass plate, rather than on the customary rotating cloth disc with alumina or diamond; and the emery paper is kept wet with methanol during polishing. Final polishing and etching

are accomplished with an acid dichromate solution (5). (For n-type PbTe, 30 ml. of saturated $K_2Cr_2O_3$ plus 7 ml HNO_3 stirred at about 150 rpm for 1.5 minutes. For p-type PbTe-SnTe, 30 ml. of $K_2Cr_2O_3$ plus 5 ml HNO_3 stirred for 1.5 minute.) Precautions are necessary to prevent retention of etch solution in the pores of the element. This involves washing ultrasonically after polishing to remove debris and again after etching to remove the etch solution; use of a detergent-wetting agent such as Alconox facilitates washing.

B. Observations

Microstructures of unbonded elements have already been shown (Figs. 7 and 8). The ability of the technique described above to preserve the bond region for examination is illustrated in Figs. 16 and 17. Fig. 17 also shows the consequences of inadequate removal of etchant trapped in the pores. The area which cannot be observed in the specimen of Fig. 17 is about two microns wide and separates the apparent surface of the element from that of the electrode (this area and the electrode are out of focus in Fig. 17). This specimen has no thermal history other than bonding. While the groove at the interface in Fig. 16 appears quite wide, a microscope can be focussed as far into the bond region as is shown in Fig. 17.

The effects of high temperature annealing on an unbonded element are illustrated in Fig. 18. Seventy hours at $700^\circ C$ did not produce any appreciable change in the microstructure of this element, and no appreciable changes in the Seebeck voltage and room temperature resistivity. The region of extensive porosity in the center of the element (Fig. 18a) is not unexpected in a cold-pressed specimen where frictional forces from the die tend to produce higher pressures and greater densification at the periphery and ends of the specimen.

Figure 19 shows the bond region of an n-type element bonded to W which was held 500 hours at $600^\circ C$. This represents a fairly severe test of the stability of the bond, and it is encouraging to note the apparent absence of any gross metallurgical changes. (Contact resistance increased four-fold while bulk resistivity decreased about 7%; other properties are not available at this writing.) There were only a few scattered indications of grain growth and no cracks or other defects. The black lens-shaped areas at the bottom center of Fig. 19a are grooves caused by preferential etching of too-deep scratches.

V. CONCLUSIONS

Efforts during this quarter have been in two main areas: characterization and evaluation of measuring techniques and of thermoelements; and refinement and evaluation of diffusion bonding procedures. The following conclusive statements can be made on the basis of these investigations:

1. Resistivity measurements (room temperature and as a function of temperature) are subject to a random error of $\pm 20\%$; however, adequate precision can be obtained from 8 - 10 repetitions.

2. Measurements of the Seebeck voltage are subject to quite small errors, of the order of 1 - 2%.

3. The cold-pressed and sintered thermoelements which have been used are 97% and 90% of theoretical density for n-type PbTe and p-type PbTe_{.5}-SnTe_{.5}, respectively. Microstructural examination confirms the presence of considerable porosity.

4. Preliminary results of vacuum fusion analysis show oxygen to be the major gaseous impurity in both types of element: n-type contain about 80 ppm and p-type about 300 ppm.

5. The pressure-diffusion bonding process for W contacts to n-type PbTe has been developed to the point where very low resistance ($5 - 10 \mu \Omega$) bonds can be reproducibly fabricated.

6. Preliminary measurements indicate that the contact resistance of W on n-type PbTe has a positive temperature dependence of approximately the same magnitude as the bulk resistance.

7. The presence of large amounts of oxygen in p-type PbTe-SnTe thermoelements apparently prevents formation of diffusion bonds to W and interferes with SnTe brazing unless very thick braze layers are used.

8. A metallographic preparation procedure has been developed to allow optical examination of bonded elements in the bond region, and of over-all microstructures of unbonded and bonded elements.

9. Examination of a few elements with different treatments indicates no appreciable diffusion zone in a diffusion bonded (W on n-type) after 500 hours at 600°C and no cracking or appreciable grain growth; as-bonded elements show a similar lack of deleterious metallurgical effects; 70 hours at 700°C produced no important structural or electrical changes in an n-type element.

VI. FUTURE WORK

In the next quarter the following areas will be investigated:

1. Evaluate bonding procedures for p-type PbTe-SnTe. Equal emphasis will be placed on an evaluation of the Ta-SnTe braze bonding and W diffusion bonding techniques. The bonding study will be supported by an effort to evaluate by both physical and chemical means the inherent properties of the p-type material which may adversely affect bonding.

2. Extensive testing of bonded elements will be carried out. More complete life test and thermal cycling information will be obtained. Electron microprobe analyses will be made on these elements to clearly define chemical stability of the bond.

3. Design a multi-life test station for bonded couples which may be used with digital data acquisition equipment for monitoring thermoelectric properties.

4. Analyze and evaluate bulk thermoelements both physically and mechanically.

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FIGURE CAPTIONS

- Fig. 1 Temperature variation of resistivity of unbonded n-type PbTe elements.
- Fig. 2 Temperature variation of resistivity of unbonded p-type PbTe-SnTe elements.
- Fig. 3 Seebeck voltage as a function of temperature of unbonded n-type PbTe elements.
- Fig. 4 Seebeck voltage as a function of temperature of unbonded p-type PbTe-SnTe elements.
- Fig. 5 Sections of n-type PbTe thermoelement.
a. Note large pore-free areas. x9.
b. Unetched microsection. x100.
- Fig. 6 Sections of p-type PbTe-SnTe thermoelements.
a. Note lack of regularity in pore structure compared to n-type. x9.
b. Unetched microsection. Note irregular dispersion of pores and more angular shape. x100.
- Fig. 7 Etched microsection of n-type PbTe element. Note psuedo-grain bounded by pores, duplex grain size and pores at grain boundary intersections. x140.
- Fig. 8 Etched microsection of p-type PbTe-SnTe element; 90% of theoretical density. Hindrance of grain growth by porosity is apparent. Compare to Fig. 7. x100.
- Fig. 9 Temperature variation of resistivity of n-type PbTe bonded elements compared with unbonded Tungsten electrodes.
- Fig. 10 Seebeck voltage of W-bonded n-type PbTe elements compared to unbonded.
- Fig. 11 Variation of contact resistivty with temperature of diffused W electrodes on n-type PbTe.

- Fig. 12 Variation of contact resistivity with temperature of W electrodes on n-type PbTe.
- Fig. 13 Variation of bulk resistivity with temperature of n-type PbTe elements.
a. Unbonded
b. Bonded to W electrodes.
- Fig. 14 Tungsten electrode (at top) diffusion-bonded to n-type PbTe. Polished with 5 μ alumina; shows grooving at bond. x200.
- Fig. 15 Tungsten on n-type PbTe (at bottom). Surface is 600 grit SiC, unetched. The excellent contact is evident along the thin black line at the center. x500.
- Fig. 16 Tungsten diffusion bonded to p-type PbTe-SnTe. Polished-etched with dichromate solution. Retention of element structure very close to interface and good surface finish of element are shown. x200.
- Fig. 17 N-type PbTe bonded to W. Focus is on element at the interface, Marks are stains from etchant retained in pores, one of which can be seen terminating a grain boundary and intersecting the element contact surface. x1000.
- Fig. 18 Unbonded n-type PbTe thermoelement annealed 70 hours at 700°C. Compare with Figs. 5a and 7.
a. Unetched, 600 grit surface. x9
b. Dichromate polish-etch. x100
- Fig. 19 Tungsten diffusion bonded n-type PbTe element. Annealed at 600°C for 500 hours.
a. Etched, electrode at top. x100
b. Etched, focussed on element. Interface is at top. Apparent absence of diffusion or precipitation is obvious. The dark specks parallel to the interface at top left are pores. x500.

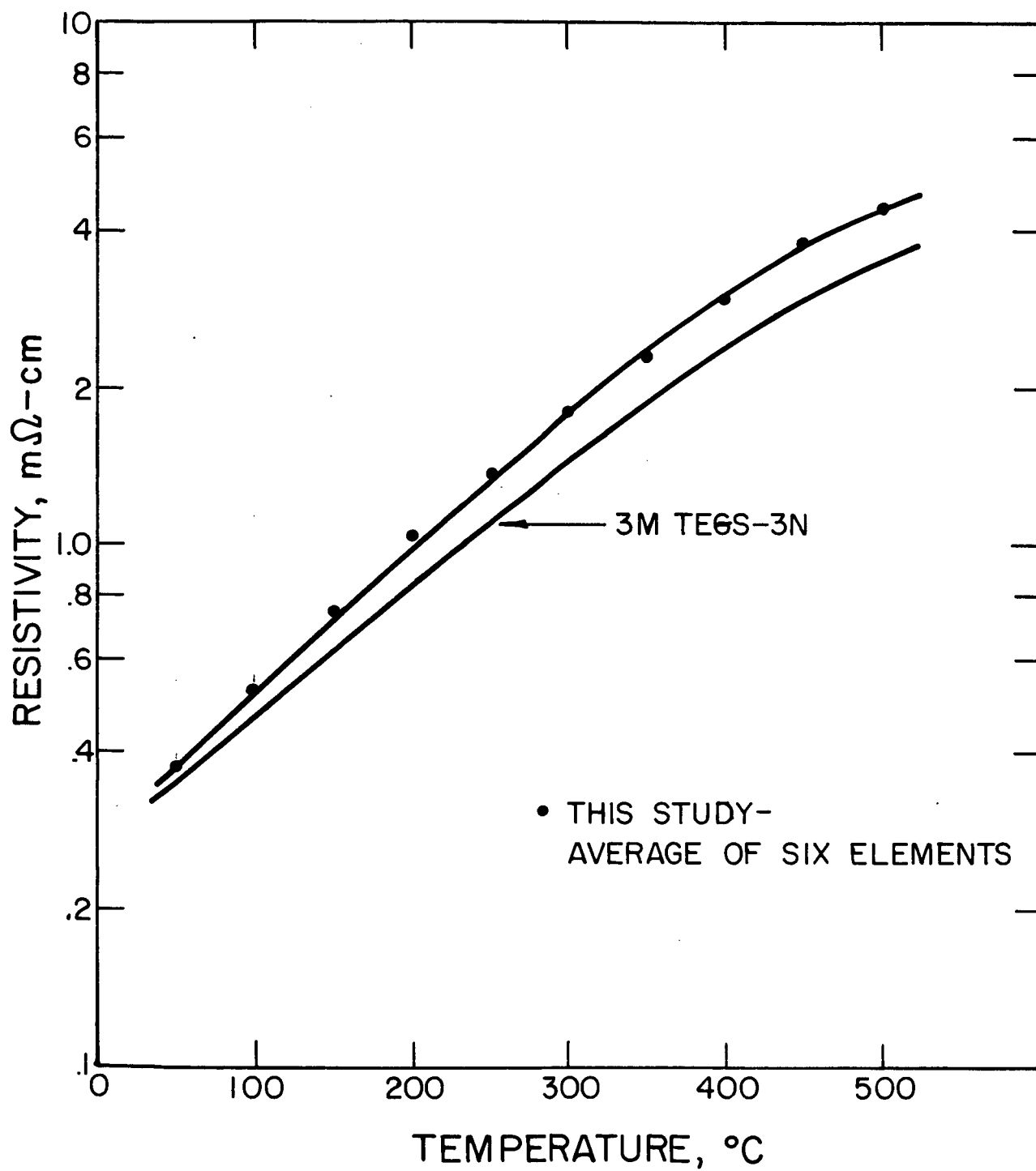


Fig. 1

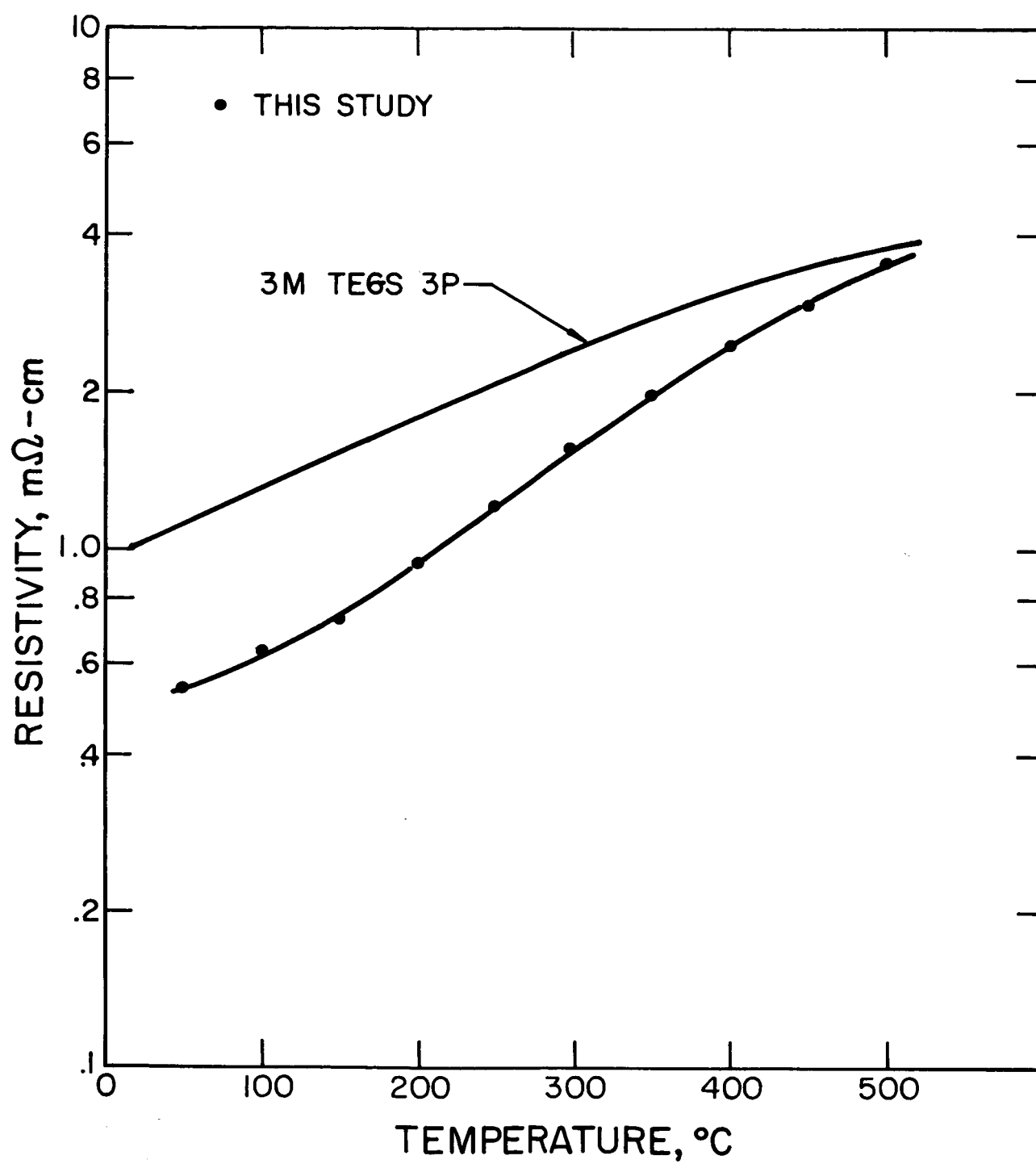


Fig. 2

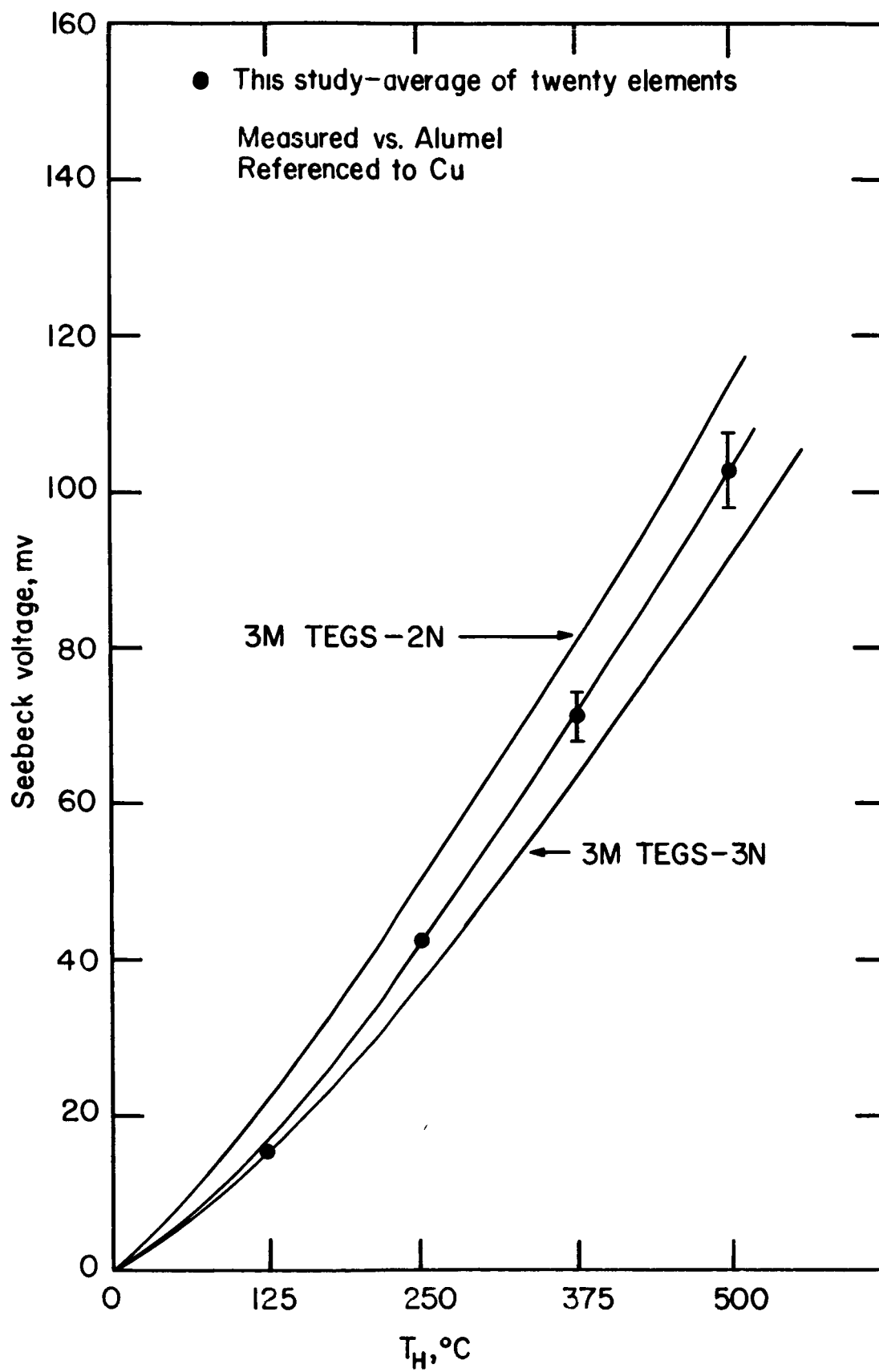


Fig. 3

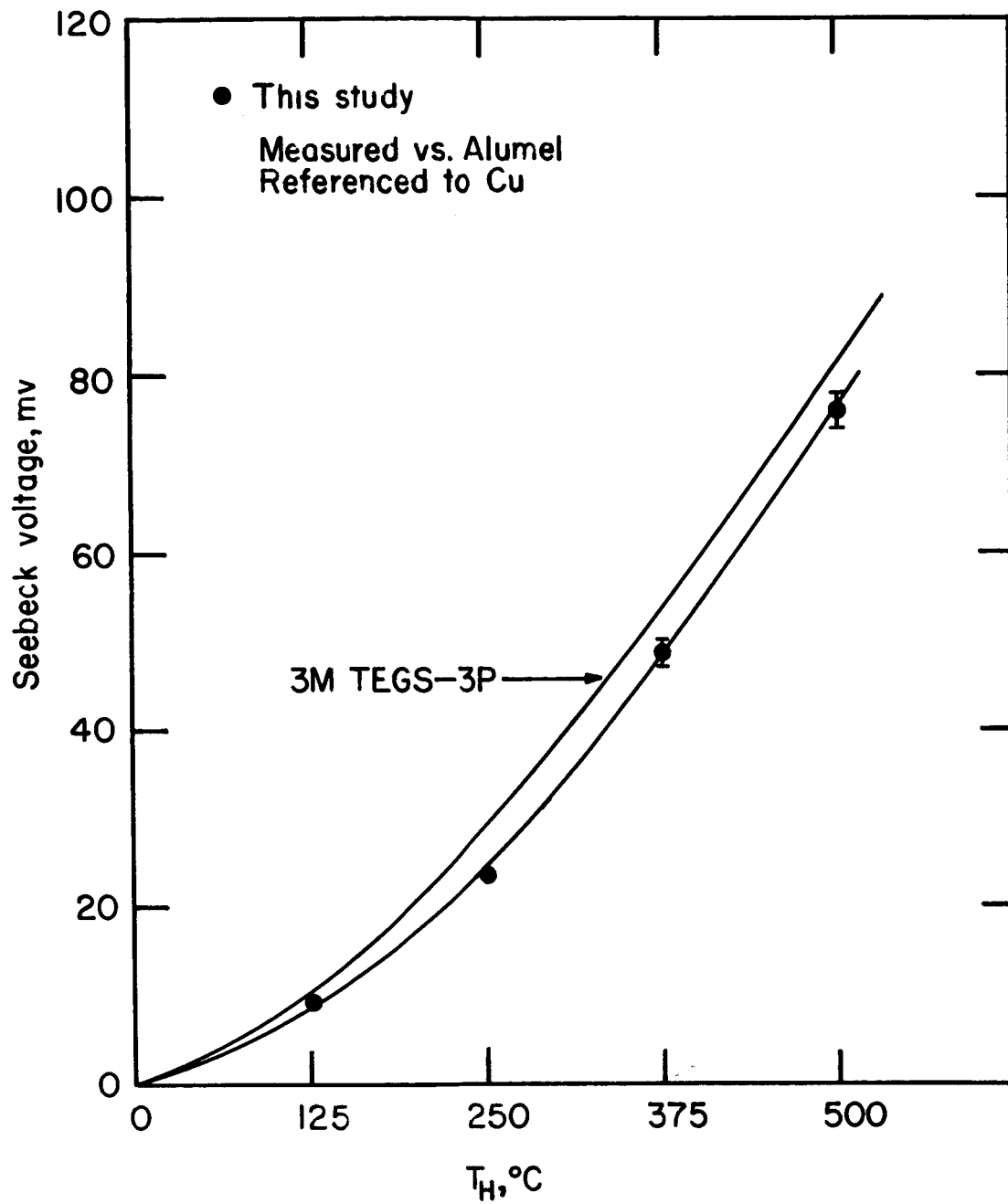
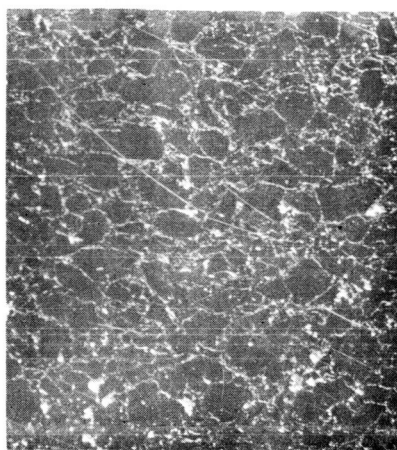
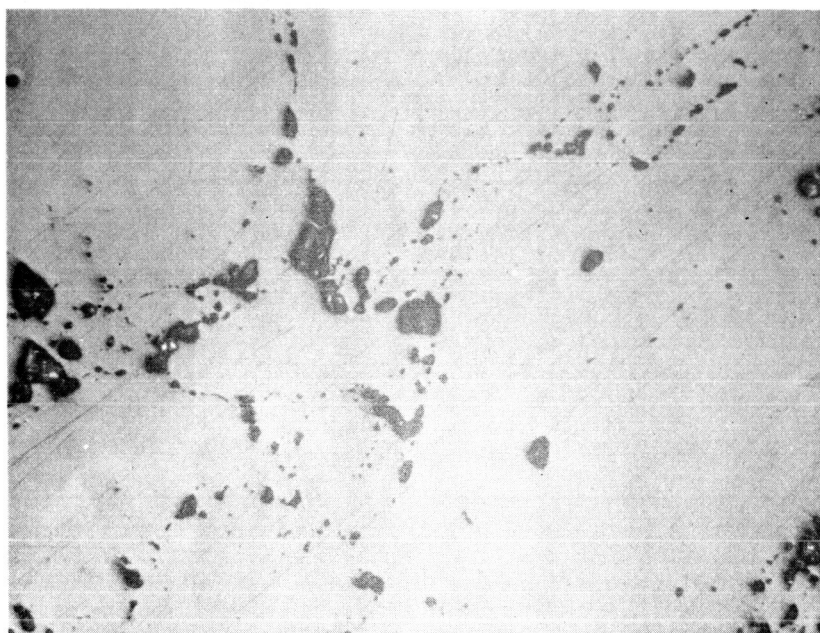


Fig. 4



a

Fig. 5

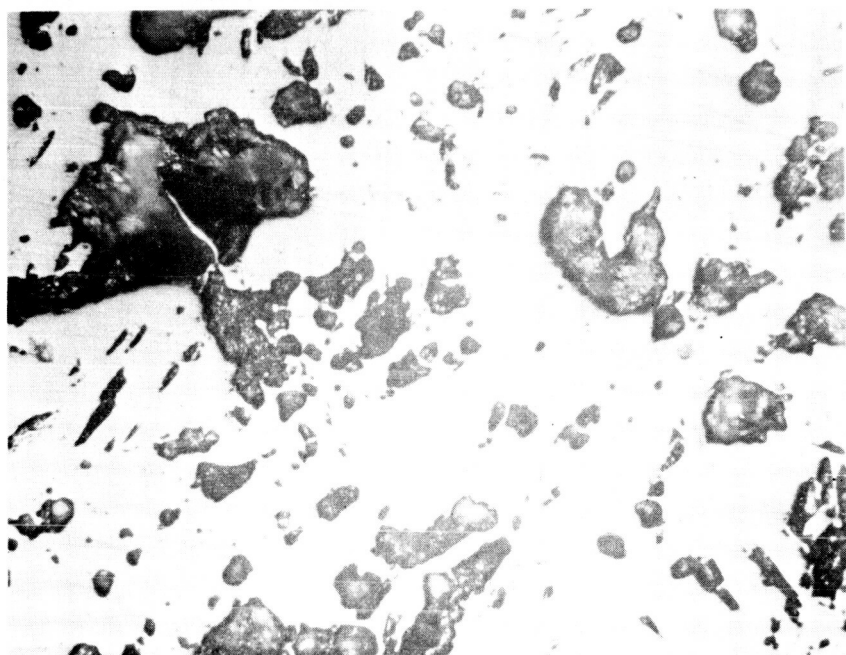


b



Fig. 6

a



b

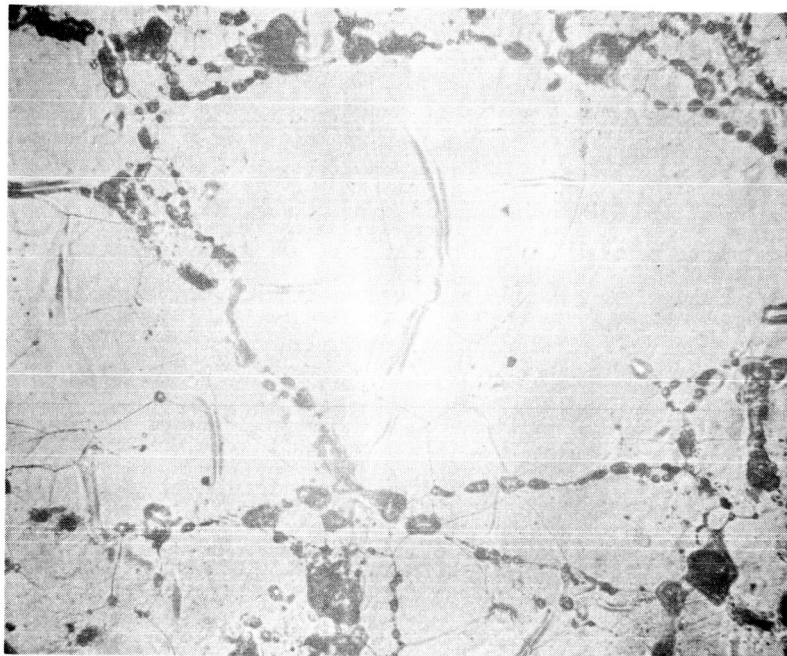


Fig. 7

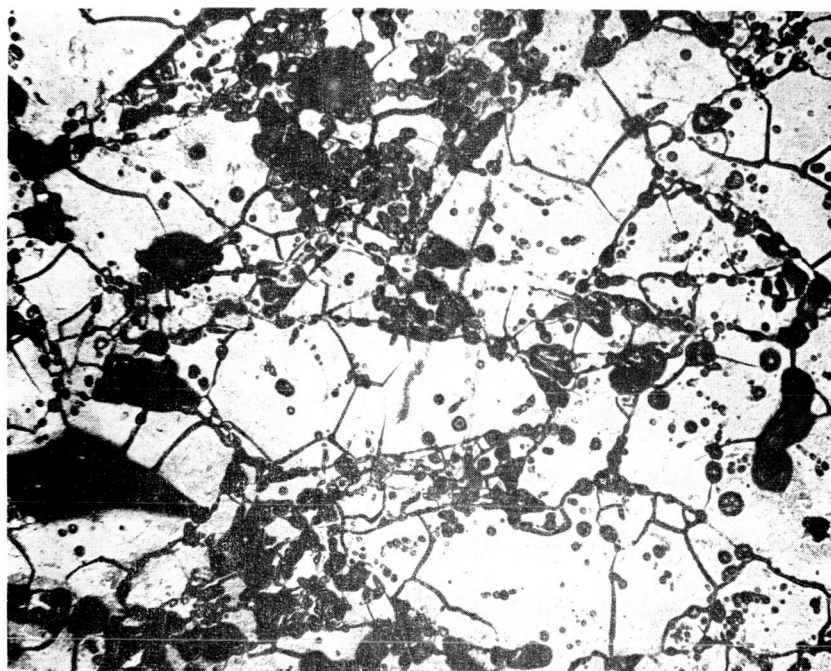


Fig. 8

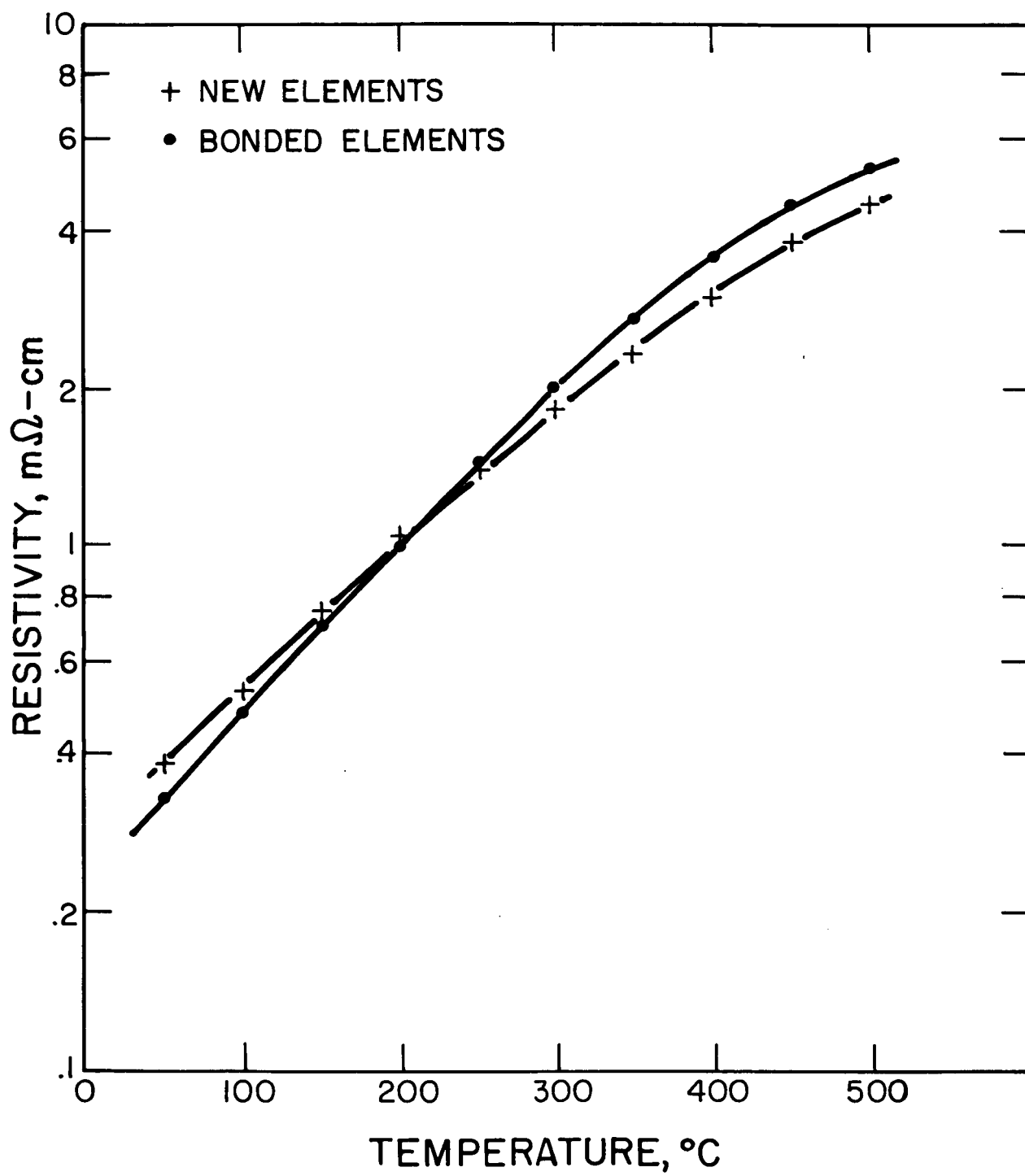


Fig. 9

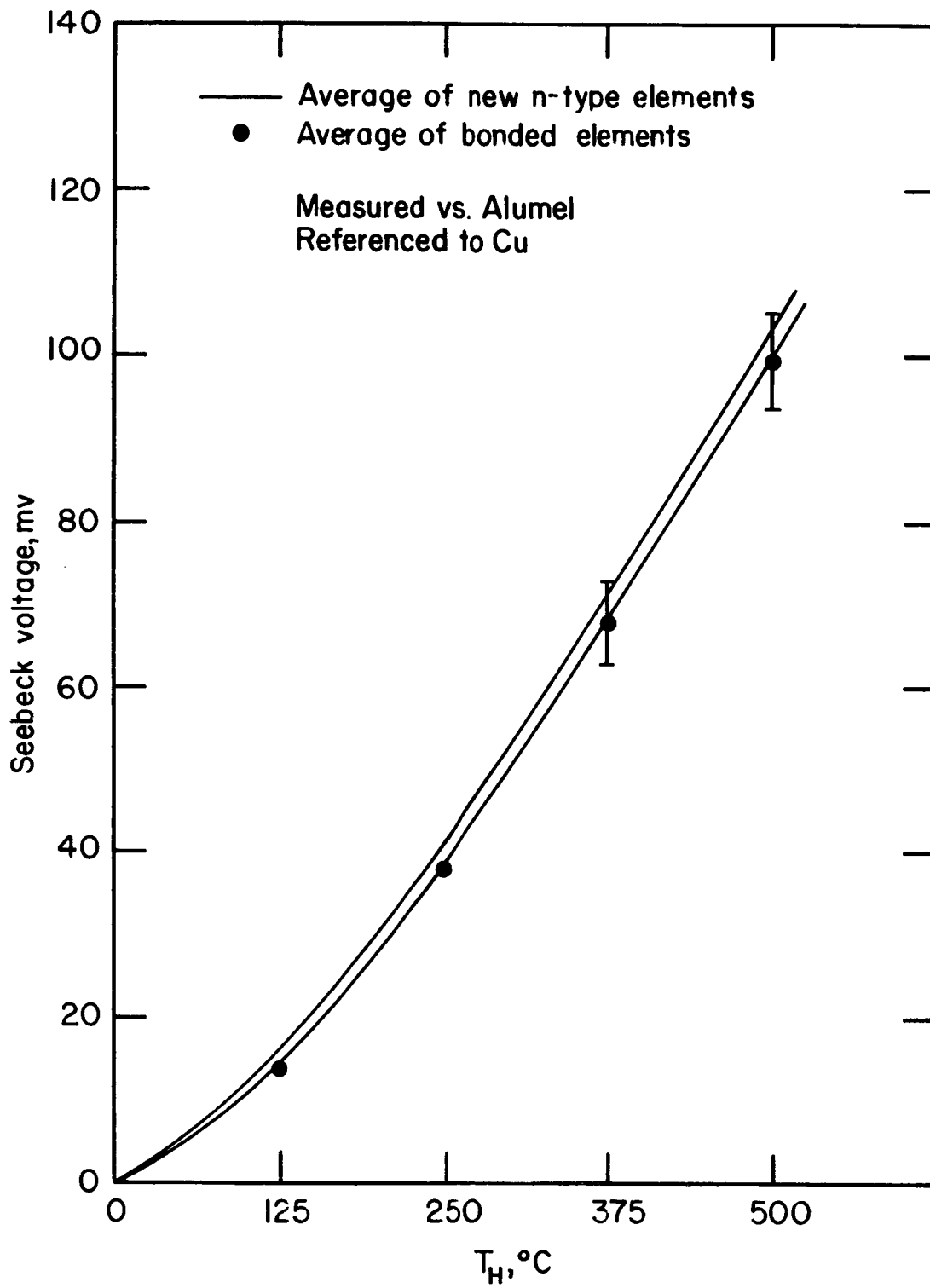


Fig. 10

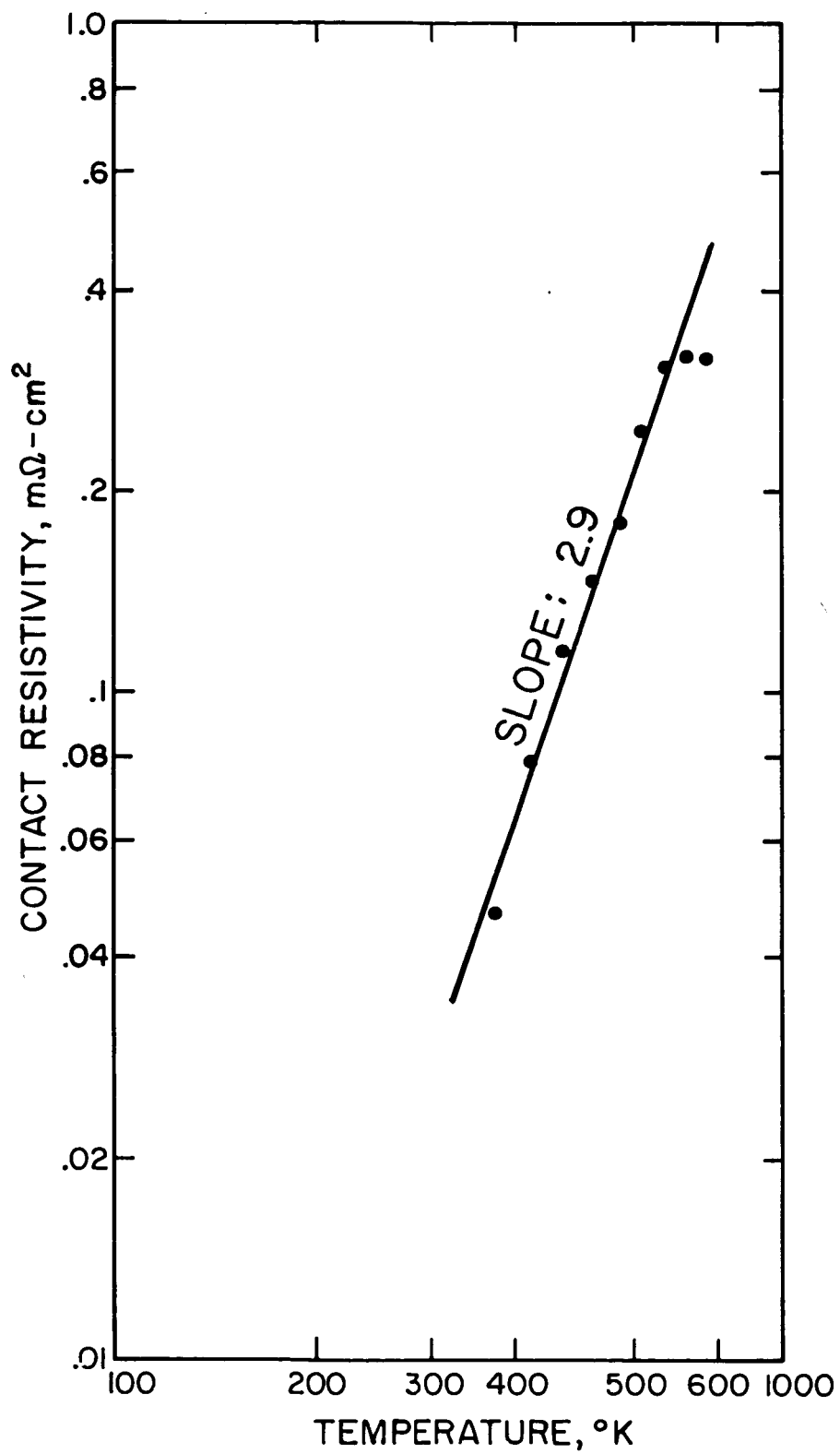


Fig. 11

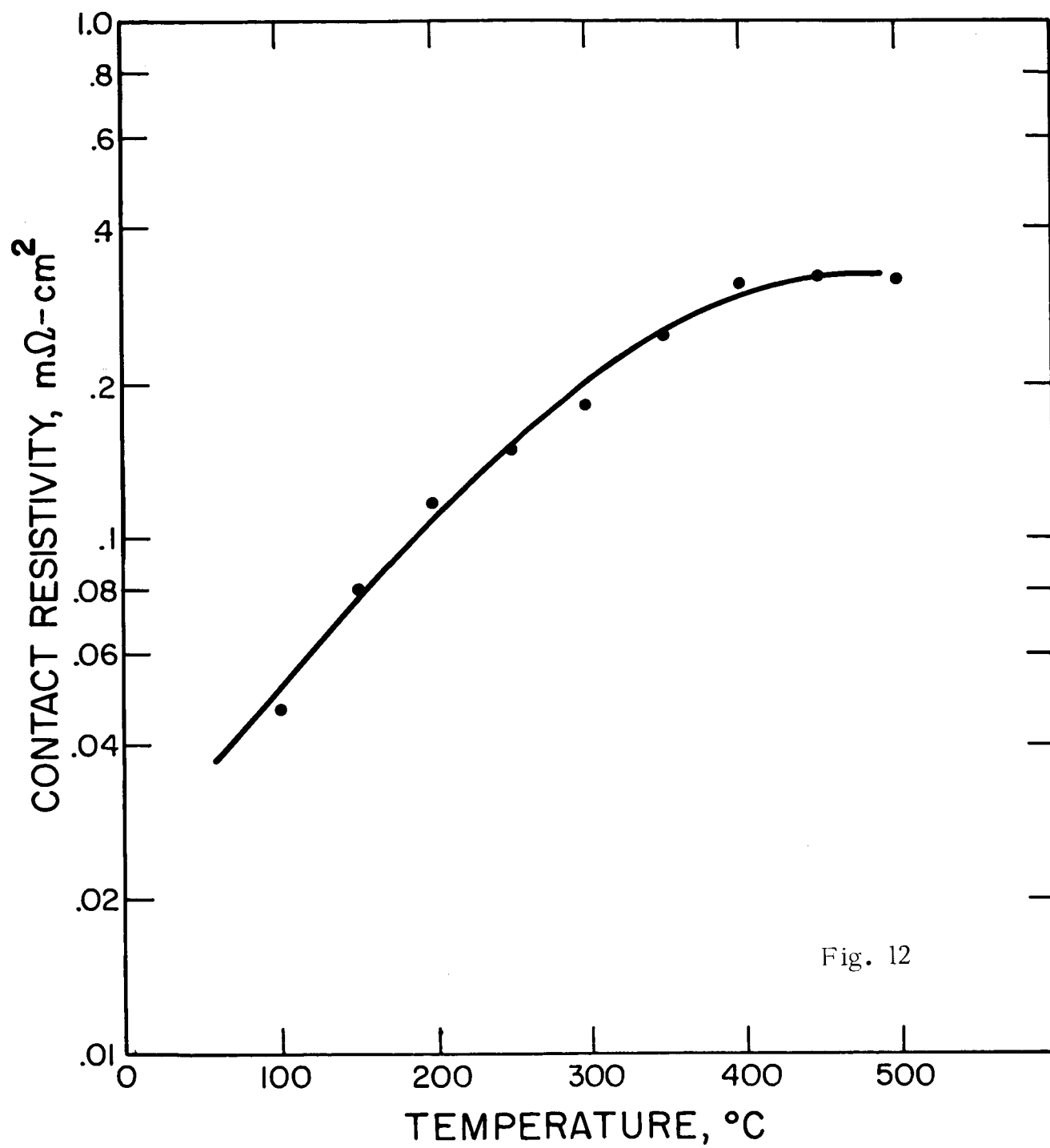
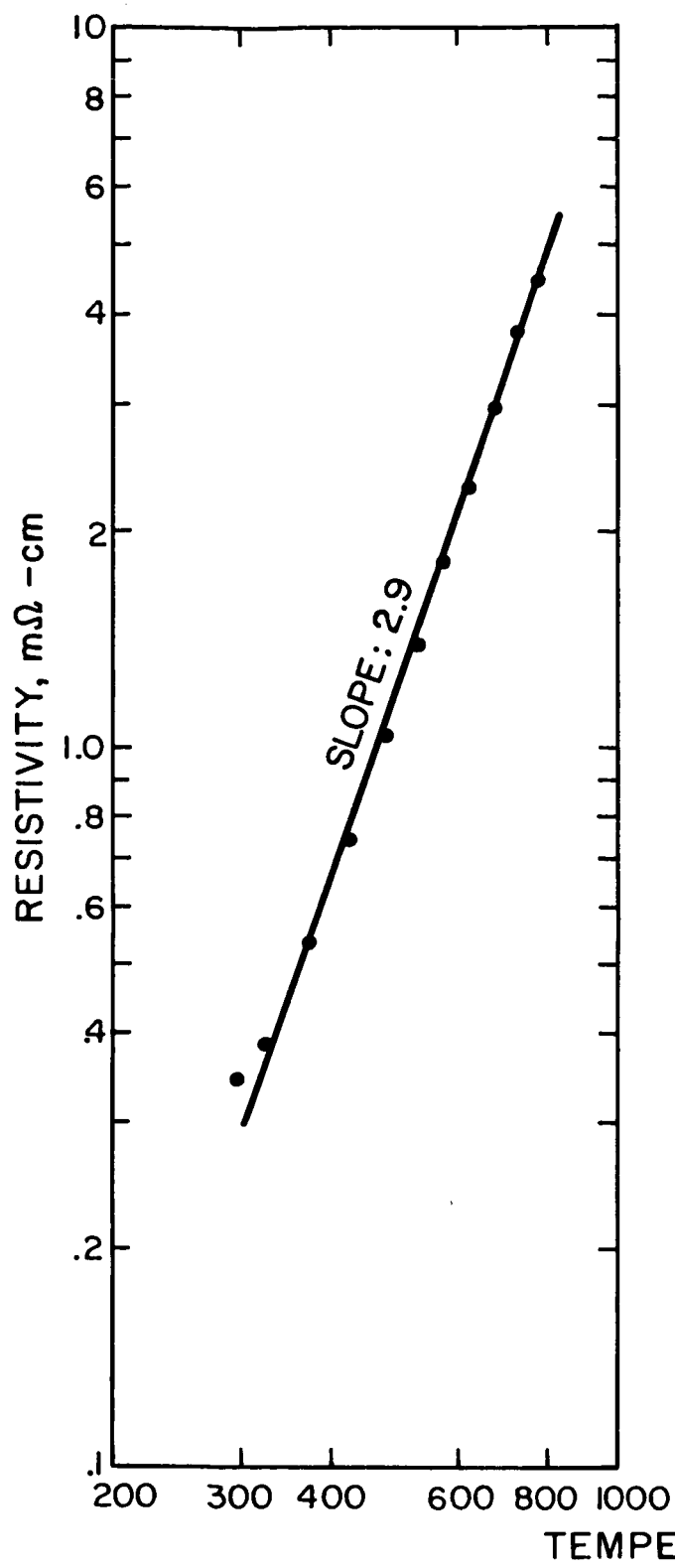
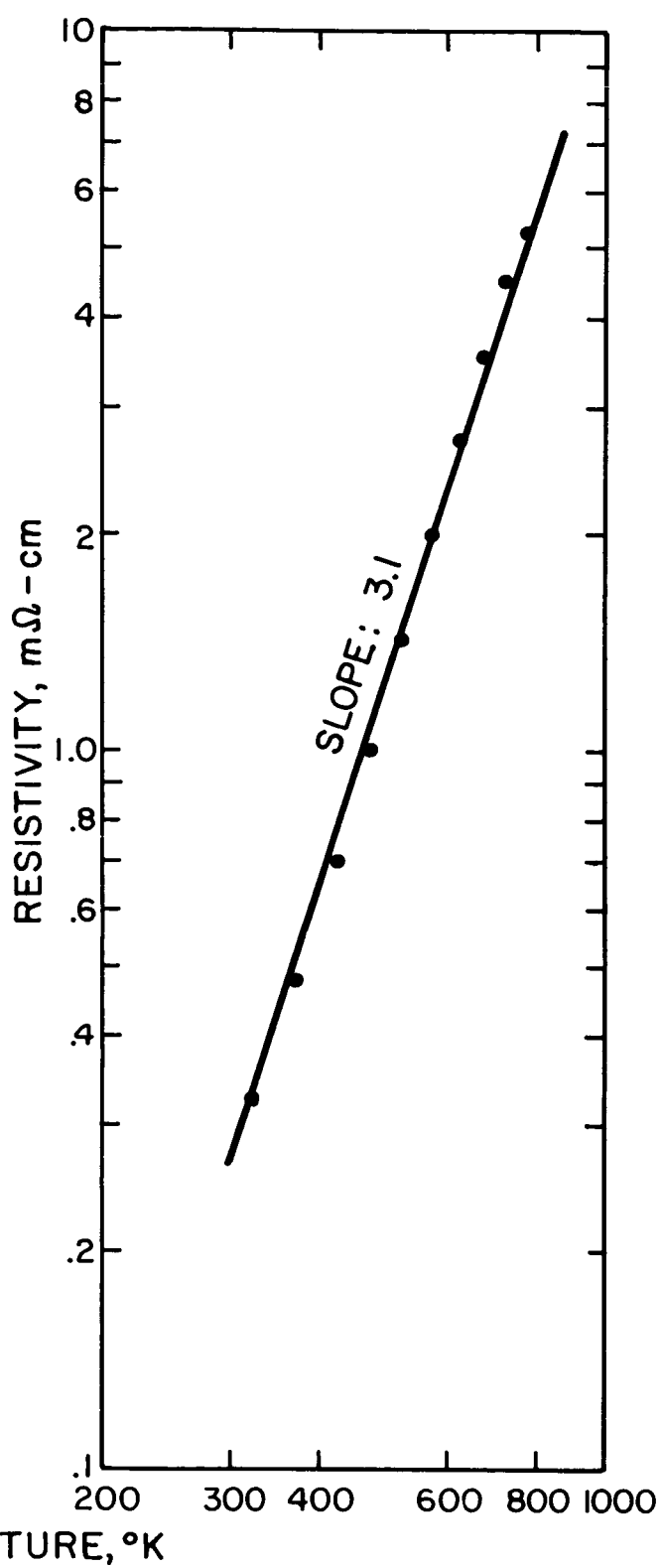


Fig. 12



a

Fig. 13



b

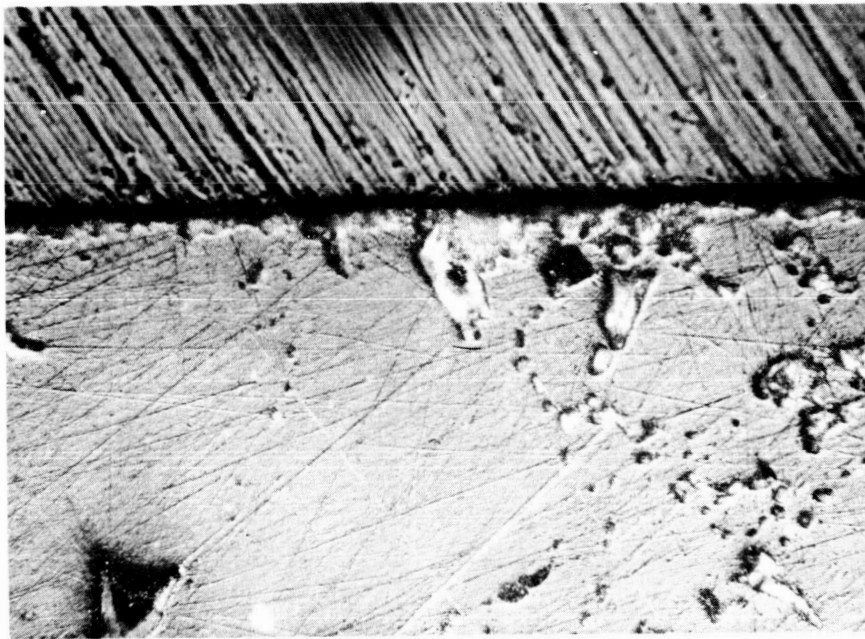


Fig. 14



Fig. 15

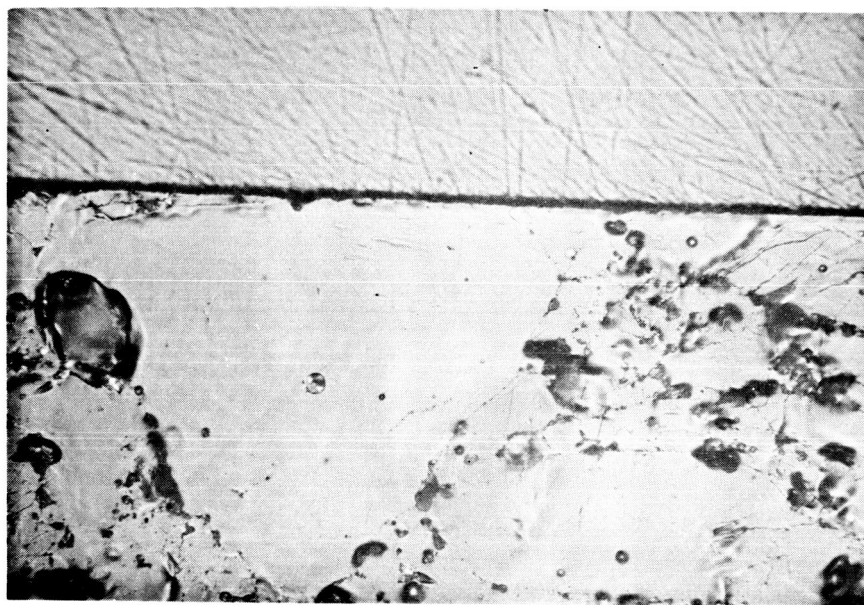


Fig. 16

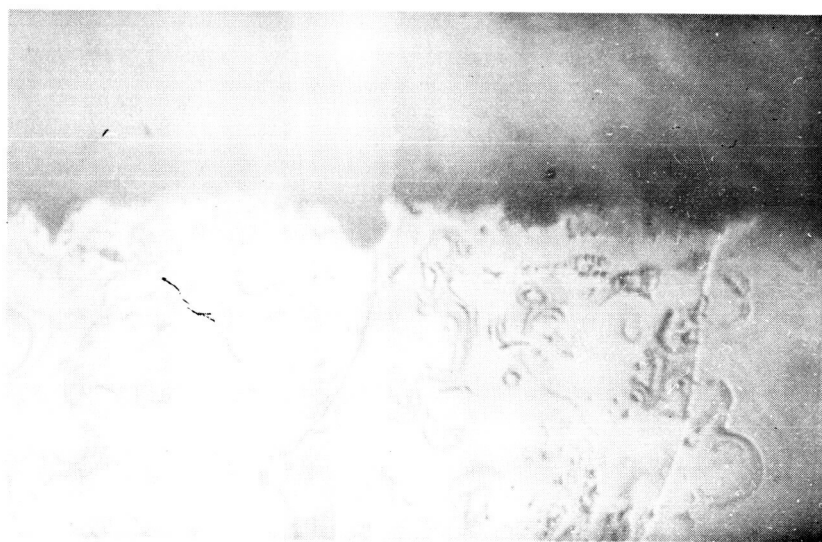


Fig. 17

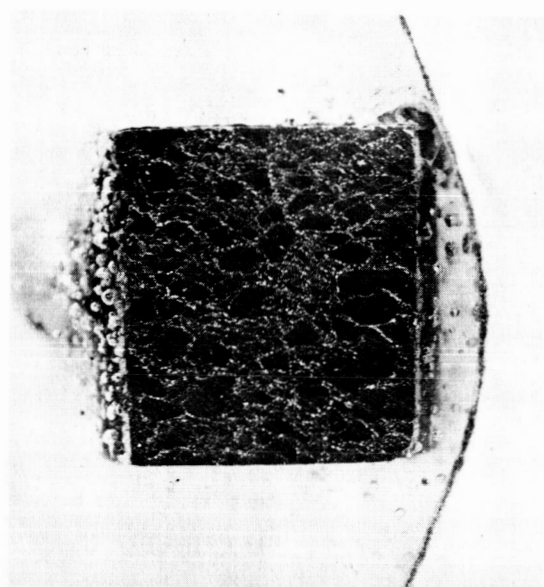
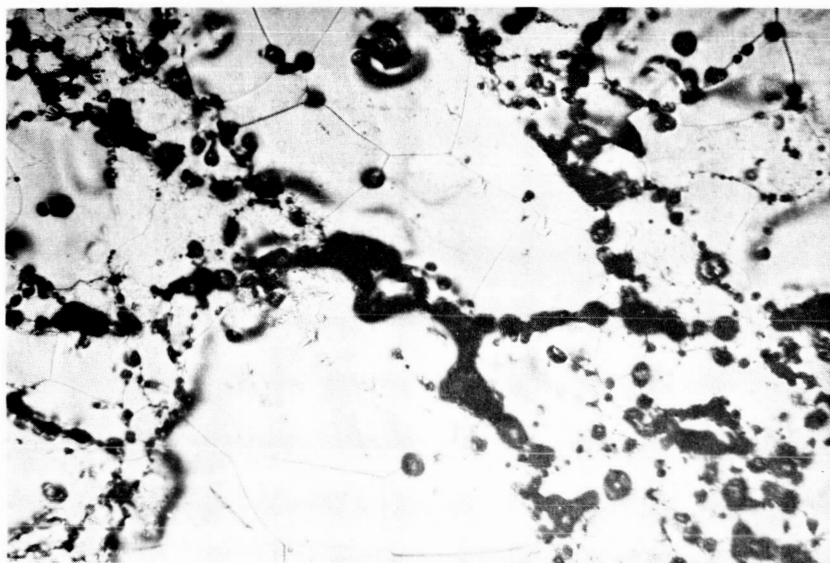


Fig. 18

a



b

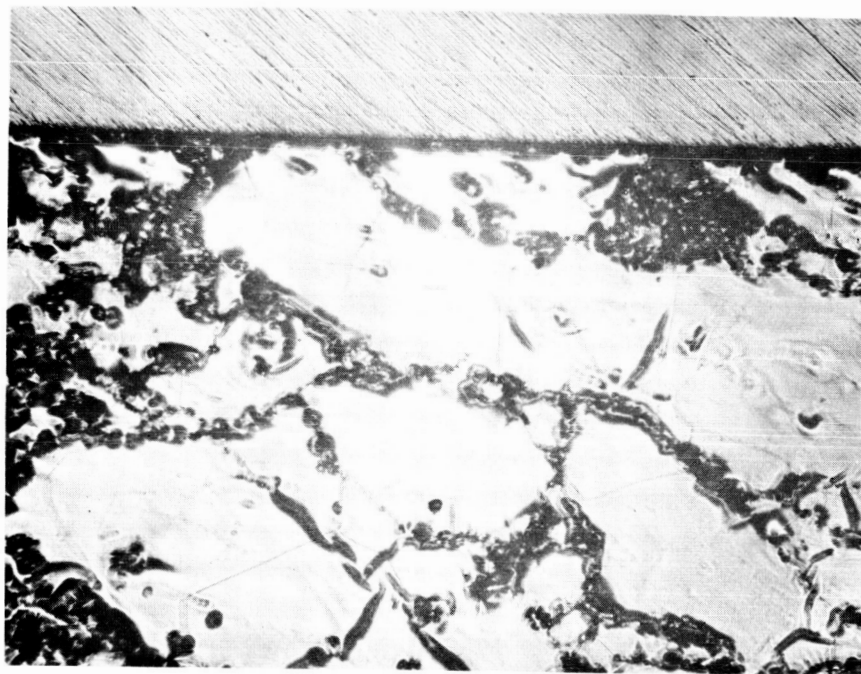


Fig. 19

a



b

FINANCIAL STATEMENT

| | <u>1st Quarter</u> | <u>Budget</u> | <u>Balance</u> |
|---------------------------|--------------------|---------------|----------------|
| Direct Labor | \$2,510 | \$12,442 | \$ 9,932 |
| Overhead | 3,137 | 15,553 | 12,416 |
| Direct Materials | 849 | 4,195 | 3,346 |
| Travel | <u>0</u> | <u>400</u> | <u>400</u> |
| Total Cost | \$6,496 | \$32,590 | \$26,094 |
| Fixed Fee | <u>454</u> | <u>2,282</u> | <u>1,828</u> |
| Total cost plus fixed fee | \$6,950 | \$34,872 | \$27,922 |